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CONTRACT REPORT NO. OSQ 82-00085

DETERMINATION OF RADIUM 226 ACTIVITIES IN URANIUM BEARING REFERENCE MATERIALS FOR CERTIFICATION PURPOSES

FINAL REPORT

BY

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Extraction Procedure

Four bottles of CCRM samples were received by mail in September 1982. These carried the designations, DL-1A, DH-1A, BL-4A and BL-5.

The procedure adopted for each material was as follows. The bottle was opened and the entire contents emptied into a clean, dry Teflon beaker and thoroughly stirred with a glass rod. Approximately 1g was weighed into a 100 ml platinum crucible (approximately 4g in the case of DL-1A). To the dry powder, 0.5 ml of a solution of ^{133}Ba tracer was added (which yielded - 7000 cpm on the gamma ray spectrometer). Ten drops of concentrated nitric acid was added and sufficient hydrofluoric acid to completely wet the sample. The crucible was set on a hot plate and allowed to fume to almost complete dryness.

Sill's fusion (Sill et al. 1974) method was used to bring the sample into solution. Four times as much anhydrous potassium fluoride by weight was mixed with the sample. The mixture was heated with a blast burner until a clear amber coloured melt was obtained. The flux was cooled rapidly to promote cracking. Concentrated sulphuric acid was added dropwise until the melt was covered with the acid. When bubbling had subsided, the crucible was transferred to the hot plate and heated to complete the transposition to the sulphate regime. When the sulphuric acid started to fume, the crucible was placed over the blast burner and cautiously heated to avoid sputtering, approximately 2g of anhydrous sodium sulphate was then added. After further heating, a quiescent clear pyrosulphate melt was obtained having a deep amber colour.

After cooling, the melt was added to approximately 60 ml of hot (- 80° C) 1N hydrochloric acid with stirring.

After the melt had dissolved, the solution was examined carefully for any evidence of undissolved grains and then filtered through a 0.45 micron millipore filter. The membrane was mounted on a plastic disc and measured for alpha particle activity. These measurements always gave null results.

To the hot solution of the sample was added dropwise three 0.5 ml portions of 0.1 M lead nitrate solution. After boiling for several minutes, the beaker was set in a water bath and left to cool for 30 minutes. The lead sulphate precipitate was separated by centrifuging and dissolved in 0.25 M alkaline disodium EDTA solution. To this solution was added 0.3 ml of 0.01 M barium nitrate. Barium sulphate was precipitated by dropwise addition of glacial acetic acid.

The barium sulphate was collected on a 0.1 micron 'Tuffryn' filter, and washed with 1% sulphuric acid followed by ethanol.

In the case of higher activity samples BL-4A and BL-5, aliquots of the EDTA solution were taken to reduce the activity on the final radium extract. Extracts of the NBS radium standard were prepared in the same way omitting the fusion procedure.

Counting Procedure

The filter membrane holder was designed and constructed at the University. The lower part of the filtration apparatus forms an integral part of the vacuum chamber used for counting. In this way the circular area defined by the retaining ring is maintained unchanged during filtration and counting. The membrane was not

handled at all from the collection of $Ba/RaSO_4$ until the conclusion of alpha spectrometry.

The counting chamber consisted of a hollow aluminium cylinder sealed at the top by a flange carrying a 450mm². ORTEC surface barrier detector, and at the bottom by the teflon filtration sub-assembly. The design was intended to maintain optimum coaxial geometry.

The output from the surface barrier detector was amplified by a modified 'The Nucleus' model 5300 alpha spectrometer. The amplified signals were analyzed using 512 channels of an 'Inotech' model 5300 multi-channel analyzer. The gain and zero of the MCA were adjusted so that the 512 channels covered the interval 0.24 to 10 MeV energy interval. Counts were collected immediately following radium extraction over periods varying from about 45 minutes to eight hours depending on various factors (discussed in the subsequent paragraph on data analysis). At the completion of alpha counting, the integral over the radium 226 peak was read out using the "region-of-interest" mechanism from channels 24 to 227. The entire pulse height spectrum was printed out on a teletype so that tailing corrections from daughter nuclides could be made if required.

The ^{133}Ba recovery was determined by placing the source on an ORTEC WIN-15 Ge(Li) gamma ray detector. Counts were accumulated from the 356 keV ^{133}Ba peak corrected for the continuum and ^{214}Bi contribution. The yield from the source was compared with the count from a standard planchet into which 0.5 ml of the spike solution had been pipetted and evaporated under a heat lamp.

The alpha background was measured by preparing blanks using the same chemical procedure as for the samples. Four such blanks yielded count rates of 0.01±0.02 cpm.

Data Analysis

a) Introduction

In order to achieve optimum results, we were obliged to deviate from the contract specifications to some extent. In particular, it was not always possible to accumulate counts to the desired 0.41% one sigma level uncertainty in the counts (- 60,000 counts). The reasons for this were:

a) The growth of ^{222}Rn daughter in the extract, after a few hours, contributes counts within the ^{226}Ra radium window. This can be corrected for, to some extent, by fitting a function of the form $y = a_1 (a_2 + \tan^{-1} a_3(x - a_4))$ (Bland 1981) (where y are the counts per channel and x is the channel no.) and extrapolating back to the channels occupied by the radium peak. Unless the source is very thin the uncertainty in the correction exceeds the uncertainty that would have been due to less counts and a corresponding reduction in radon in-growth.

b) Prolonged exposure to high count rates, e.g. in the case of BL-5, causes contamination of the surface barrier detector and a rise in the background counts. Corrections for such background would nullify the advantages of long counting times. Alternatively replacement with a new detector would cause changes in the response factor (and the cost of two detectors would exceed the entire contract cost).

c) In the case of some of the samples ^{224}Ra and ^{223}Ra, plus their

daughters further complicate the spectrum. By the time these radium isotopes decay with storage, ^{226}Ra daughters would grow in to almost equilibrium conditions.

As a consequence of the above factors, the contractor has terminated the counting of each sub-sample at a time when he believed the optimum accuracy would have been achieved, i.e. a compromise between Poissonian error and corrections due to daughters. Due to the relatively low activity of the sample DL-1A, much longer counting times were necessary and, for convenience, were counted overnight or over weekends. The corresponding tailing corrections are noted in brackets under the peak counts for each sub-sample.

b) Treatment of Recovery Data

C_{ST} = the counts from ^{113}Ba standard

C_{SA} = counts from the ^{133}Ba in the sub-sample

C_{BK} = counts due to background

Time intervals are the same in each case. The recovery R, is given by:

$$R = \frac{C_{SA} - C_{BK}}{C_{ST} - C_{BK}}$$

where the variance is given by

$$\sigma_R = R \left[\frac{(C_{SA} + C_{BK})}{(C_{SA} + C_{BK})^2} + \frac{(C_{ST} + C_{BK})}{(C_{SA} + C_{BK})^2} \right]^{1/2}$$

By accumulating - 70,000 counts on each measurement, recoveries were measured to an accuracy of 0.54%.

c) Derivation of Corrected Count Rate for Each Sub-sample

The corrected count rate, CR, is given by

$$CR = \frac{\text{Counts (corrected for tailing)}}{\text{Time x Recovery (R) x Weight}}$$

with a variance of:

$$\sigma_{CR} = CR\left[\frac{1}{\text{Counts}} + \frac{\sigma_R^2}{R^2} + \frac{\sigma^2_W}{W^2}\right]^{1/2}$$

$\frac{\sigma_W^2}{W^2}$ was determined by repeated weighing to be approximately 1×10^{-6} for all sub-samples.

d) Calculation of Weighted Mean for Each Group of Sub-samples

Each corrected count rate CR_i is weighted by $\frac{1}{\sigma_{CR_i}^2}$ thus the weighted mean is given by

$$\mu = \frac{\sum \frac{CR_i}{\sigma_{CR_i}^2}}{\sum \frac{1}{\sigma_{CR_i}^2}}$$

The weighted variance is calculated (Bevington 1969) from the expression:

$$\sigma_\mu^2 = \frac{\sigma^2}{N}$$

where

$$\sigma^2 = \frac{N \sum [W(CR_i - \overline{CR})^2]}{(N-1) \sum W}$$

and

$$W = \frac{1}{\sigma_{CR_i}^2}$$

e) Calculation of Mean Activity of Samples Relative to NBS Standard

The mean activity of the sample is obtained from the expression:

$$A = \frac{CR_S}{CR_{ST}} \times S$$

where CR_S is the mean corrected count rate per gram of the sample, CR_{ST} is the mean corrected count rate of one ml of the NBS standard, and S is the activity assumed for that quantity of the NBS standard.

Activity of the NBS ^{226}Ra Standard

According to the National Bureau of Standards certificate (copy attached) as of September 1, 1967, the ampoule contained 0.4957 micrograms. This was determined by comparing it's rate of gamma ray emission with those of a 1957 series of standards. Since most of our determinations were made around mid-November 1982, a correction must be made for the decay of the isotope, using the following relationship.

$$W(t) = W(o)\ e^{-\lambda t}$$

where $W(t)$ = present weight of ^{226}Ra

$W(o)$ = weight as of September 1, 1967

λ = decay constant of ^{226}Ra

t = elapsed time

and $\lambda = \frac{\ln 2}{\tau_{1/2}}$

where τ is the half-life of ^{226}Ra = 1600 years

whence W(t) = 0.4925 micrograms.

For the purposes of measurement, the contents of the ampoule were diluted in a volumetric flask to yield a standard solution containing $\frac{1}{500}$ of the total activity per ml.

Conclusions

Final values for these determinations are given in Table 6. The error in the NBS standard has not been included in the error analysis. Tables 1-5 give the raw data and the values for the corrected cpm g^{-1} for each sub-sample.

Apart from whatever errors may be due to the fault of the analyst, variations in the final values may have been reducible had we been able to dedicate more resources to this project. Ideally fresh crucibles and solid state detectors should have been used for each determination, but the costs would have far exceeded the funds for this project. It is likely that the NBS standard solution is not precise enough for measurements made with the precision available from today's techniques and the production of a Canadian national radium standard would be a worthwhile project.

Calgary, January 1983

REFERENCES

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Bland, C.J. Communication presented at the Alpha Sub-Group, ICRM, Geel, Belgium (1981), to appear in Int. J. App. Rad. and Isotopes.

Bevington, P.R. "Data Reduction and Error Analysis for the Physical Sciences" McGraw-Hill (1969).

TABLE 1

DL-1A

Sub-Sample	^{226}Ra Peak Cts. (Corrected for tailing)	Time Secs.	Recovery %	Weight Aliquot g	Corrected cpm/g
1	107038	91569	80.03	4.0027	21.89
	(3005)		± 0.47		± 0.15
2	74830	64500	78.65	4.0229	22.00
	(2199)		± 0.46		± 0.15
3	70914	58000	84.06	4.0193	21.71
	(5897)		± 0.48		± 0.15
4	58250	50000	79.88	4.0129	21.81
	(1215)		± 0.47		± 0.16

Mean Counts per Minute per Gram = 21.85 ± 0.06.

TABLE 2

DH-1A

Sub-Sample	^{226}Ra Peak Cts. (Corrected for tailing)	Time Secs.	Recovery %	Weight Aliquot g	Corrected cpm/g
1	21373	3800	74.35	1.0015	453.2
	(NA)		± 0.44		± 4.1
2	9950	2000	60.35	1.0121	488.8
	(101)		± 0.38		± 5.8
3	20060	3000	83.73	1.0239	467.9
	(90)		± 0.48		± 4.3
4	73229	12000	75.81	1.0059	480.2
	(1002)		± 0.45		± 3.4

Mean Counts per Minute per Gram = 471.4 ± 7.3

TABLE 3

BL-4A

Sub-Sample	^{226}Ra Peak Cts. (Corrected for tailing)	Time Secs.	Recovery %	Weight Aliquot g	Corrected cpm/g
1	17318	9100	87.78	0.5042	257.9
	(NA)		± 0.50		± 2.5
2	16802	8800	83.90	0.5251	260.0
	(NA)		± 0.48		± 2.5
3	19190	12300	69.79	0.5274	254.3
	(722)		± 0.43		± 2.4
4	24518	12000	88.86	0.5332	258.7
	(NA)		± 0.50		± 2.2

Mean Counts per Minute per Gram = 257.7 ± 1.2

TABLE 4

BL-5

Sub-Sample	^{226}Ra Peak Cts. (Corrected for tailing)	Time Secs.	Recovery %	Weight Aliquot g	Corrected cpm/g
1	22348	1000	93.30	0.1108	12971
	(NA)		±0.52		± 114
2	24323	1000	90.69	0.1244	12936
	(NA)		±0.51		± 111
3	19816	1000	79.09	0.1112	13519
	(NA)		±0.47		± 125
4	22718	1000	94.71	0.1065	13514
	(NA)		± 0.52		± 118

Mean Counts per Minute per Gram = 13213 ± 163.

TABLE 5

NBS Radium Standard

Sub-Sample	^{226}Ra Peak Cts.	Time Secs.	Recovery %	Weight Aliquot g	Corrected cpm/g
1	21258	2000	89.96	1.1808	600.4
	(NA)		± 0.51		± 5.4
2	20193	2000	94.50	1.0761	595.7
	(NA)		± 0.53		± 5.4
3	18570	2000	89.68	1.0430	595.6
	(NA)		± 0.51		± 5.6
4	19596	2000	89.38	1.0728	613.0
	(NA)		± 0.50		± 5.6
5	19630	2000	92.85	1.0780	588.4
	(NA)		± 0.52		± 5.4

Mean Counts per Minute per Gram = 595.0 ± 2.5

Density of Standard Solution = 1.0202 ± .0001 $g.ml^{-1}$

(mean of three determinations)

∴ Mean Counts per Minute per ml = 607.0 ± 2.6

Content of Radium per ml = 0.9850 ng as of Nov. 15, 1982

(derived from NBS certificate) equivalent to 36.021 Bq.

(using interim factor of 3.657×10^{10} Bq. g^{-1}

TABLE 6

Mean Activity of Samples (as ^{226}Ra) (Derived from NBS Standard)

DL-1A	1.297	±	.007	Bq. g^{-1}
DH-1A	27.97	±	0.45	Bq. g^{-1}
BL-4A	15.29	±	0.10	Bq. g^{-1}
BL-5	784	±	10	Bq. g^{-1}

U. S. Department of Commerce
Alexander B. Trowbridge,
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material 4957
Gamma-Ray Standard
Radium—226

This standard consists of radium-226 in approximately 5 milliliters of solution in a flame-sealed glass ampoule. The solution is 5 percent by weight HNO_3.

The weight, in micrograms, of radium-226 contained in the ampoule as of September 1, 1967, was

0.495 7

* $\pm 1.8_3\%$*.

This standard was calibrated by comparing its gamma-ray-emission rate with those of a 1957 series of standards prepared from material that had been compared in the National Bureau of Standards radiation balance, with the national radium standards. The gamma-ray-emission rates were compared in a $4\pi\gamma$ ionization chamber containing argon at a pressure of 10 atmospheres.

The uncertainty, 1.8_3 percent, is the sum of 1.0_3 percent, which is the statistical error at the 99-percent confidence level ($2.58\ s_m$, where s_m is the standard error), and 0.8_0 percent, which is the maximum uncertainty due to assessable systematic errors in the 1957 series of standards and in the ionization-chamber comparisons.

This standard was calibrated in the Center for Radiation Research by members of the Radioactivity Section, W. B. Mann, Chief.

Washington, D. C. 20234
March 1, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

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